MEASUREMENT OF SURFACE PROPERTIES OF COAL USING A MODIFIED WASHBURN TECHNIQUE

Geatesh K. Tampy, Wen-Jia Chen, Michael E. Prudich and Robert L. Savage

Department of Chemical Engineering
Ohio University
Athens, Ohio 45701

Abstract

Several physical coal cleaning processes, e.g. oil agglomeration and flotation, are dependent on the surface properties of coal. One conventional method of surface characterization involves measurement of the contact angle. The Washburn method of contact angle measurement has advantages over most other techniques used to measure the contact angle of solids in powder form. This technique involves filling a vertical cylindrical tube with the powdered solid and allowing a liquid to penetrate the powder bed by capillary driving forces.

The Washburn method has been modified using fundamental equations governing fluid transport through a packed bed. The experimental methodology itself has been extended to allow for the application of an external pressure differential to supplement the capillary forces. The addition of the applied pressure differential simplifies computation of the contact angle. Contact angles for different coal/oil systems have been measured and the interfacial free energy changes have been quantified. These results have been related to performance of the coals in the oil agglomeration process.

INTRODUCTION

There are several different methods for characterizing the interaction of nonpolar and nonionic liquids with polydisperse, heterogeneous solids (like coal) in powder form. These characterization techniques often result in the calculation of a contact angle. Unfortunately, the results produced from these varying techniques often do not agree. Two of the more popular quantitative methods for measuring the contact angle in such systems are the Bartell plug method(1) and the Washburn capillary rise method(2). More recently Heertjees and Kossen(3) have suggested a different approach which involves making a compressed pellet out of the powdered solid, and measuring the height of a drop of liquid placed on the pellet. The contact angle is measured based on the height of the drop and the porosity of the plug as measured by mercury intrusion. However, Neumann and Good(4) have indicated that pelletization changes the nature of the solid surface. The Bartell method, which involves the application of an external pressure to resist the penetration of a liquid into a plug of the solid powder, is extremely cumbersome. The Washburn method, which also involves a plug of the solid powder, is much simpler to perform and involves filling a vertical glass tube with the powder and allowing the liquid to penetrate the plug aided purely by capillary forces. The rate of penetration is measured and the contact angle calculated.

The Washburn method, though simple in execution, has two major drawbacks: 1) The computation of the contact angle is based on the assumption that the powder in the tube can be described as a bundle of capillaries with circular cross-section. The Hagen-Poiseuille equation is then applied to yield,

$$\frac{dh}{dt} = \frac{R^2 \Delta P}{8 \nu h} \qquad 1)$$

where t is time, h is the height of the column of liquid in the capillary, R is the radius of the capillary, ν is the viscosity, and ΔP is the Laplace pressure, given as,

$$\Delta P = \frac{2\, \delta_{lv} \cos \theta}{R} \qquad 2)$$

where δ_{lv} is the liquid-vapor interfacial tension and θ is the contact angle. 2) The capillary radius, R, in the equation above, has to be calculated in order to determine the contact angle. The suggested methods for doing this include either conducting an experiment with a liquid which "completely wets" the surface of the powder (then the cos θ value is forced to unity and R can be directly computed) or using mercury porosimetry data to estimate the value of R (5). There are problems with both of these approaches. For a heterogeneous substance like coal, it is not easy to find a liquid which completely wets all of the chemically different fractions (both organic and mineral). Furthermore, at least two experiments are required in order to quantify the contact angle, the experiment with the completely wetting liquid and the experiment with the liquid to be characterized. The packing of the powder plug in the two experiments might not be the same, resulting in an erroneous estimation of R.

Using mercury porosimetry to estimate R has its own unique problems. The contact angle for mercury with most solids is known to lie between 130 and 140 degrees(5). Therefore, the "wetting" of coal by mercury is accompanied by an <u>increase</u> in the surface free energy. In oil agglomeration,we are looking for oils which will wet the coal surface and cause a <u>decrease</u> in the surface free energy. Keeping these conditions in mind, in the absence of an applied external force oils will spontaneously penetrate the interstices of the plug to a much greater degree, and more quickly, than mercury. The effective interstitial structure that mercury sees is not the same effective interstitial structure that the oils sees. It is this effective structure that defines the behavior of the draw up of oil by the plug.

Figure 1 shows the results of mercury porosimetry tests on two powdered coal samples, PSOC 276 and PSOC 751. The volume of mercury intrusion per gram of sample was found to increase from 0.18 ml to 1.16 ml for PSOC 276 and from 0.15 ml to 1.15 ml for PSOC 751 as the applied pressure was increased from 0 psia to 48,000 psia. Table 1 indicates the volumes per gram drawn into the same two coals for different agglomerating oils. Comparing Figure 1 and Table 1 it can be seen that a pressure of about 100 psia would have to be applied to the mercury system to cause the same amount of mercury draw-up that occurs spontaneously (at 0 psia) for the hydrocarbon oil systems.

TABLE 1

Specific Oil Draw-up for Coal Samples.

	Specific Draw-up, ml oil per gram coal		
Coal Sample	No.2 Fuel Oil	Varsol	Pentane
PSOC 276	0.88	0.90	0.92
PSOC 305	0.88	0.87	0.82
PSOC 751	0.85	0.83	0.82

EXPERIMENTAL METHOD

It is evident that before reasonable results can be expected, both limitations indicated above have to be eliminated. To do this, we first follow a procedure which has been successfully adopted to define the flow of fluid through a packed bed. These results are well documented in the literature(6,7) and are applicable for laminar flow (low Reynolds number, so that inertial forces can be neglected). This condition can be expected to exist when Laplace pressure drives the fluid. The analysis essentially involves two modifications to the Washburn procedure: 1) The radius of the circular capillary, R, is replaced by a "hydraulic radius", r, which is defined as the ratio of the area of cross-section of the pore through which the liquid penetrates to the wetted perimeter. The advantage of doing this is that r may subsequently be eliminated from the equation by using a relationship between r and the "average" particle diameter, D.

$$r = (De\phi)/6\cdot(1-e) \qquad 3)$$

where ϕ is the sphericity and is assumed to equal 0.73 for pulverized coal(8). e is the interstitial void space per unit volume of the bed, or bed porosity. 2) A tortuosity factor is used to modify the distance of fluid flow upward through the packed bed. The tortuosity factor is required because the actual distance through which the liquid flows is greater than the measured height, h. Values for this factor have been experimentally determined to lie between 2.0 and 2.5, as long as the porosity of the bed is not much greater than 0.5, and the flow is laminar. A value of 25/12 was used for the tortuosity factor in our calculations(6).

If the Laplace pressure accounts for the only force causing the draw-up of then liquid, then substitution and integration yields,

$$\frac{h^2}{t} = \frac{D\cdot\phi\cdot e\cdot \sigma_{lv}\cos\theta}{12.5\,\nu\,(1-e)} \qquad 4)$$

The above equation is not based on the assumption that the bed is a bundle of cylindrical capillaries, and also, more importantly, the velocity can be related to the particle diameter and the porosity, which is determined by measuring the quantity of liquid drawn up into the bed per unit weight of solid for each bed used.

For heterogeneous, polydisperse systems, the average diameter to be used in Equation 4 may be difficult to measure. This difficulty may be overcome by repeating the capillary plug experiment with the addition of an external pressure driving force applied in the same direction as the capillary pressure. The additional applied pressure driving force is added linearly to the Laplace pressure driving force which appears implicitly in Equation 4. This treatment results in a system of two equations with two unknowns and a new h^2/t slope is obtained which permits D to be eliminated from the resulting single equation.

RESULTS AND DISCUSSION

Three coals, PSOC 276 (Ohio #8, hvAb, 13.5% initial ash), PSOC 305 (Ohio #11, hvBb, 22.5% initial ash), and PSOC 751 (Ohio #6, hvBb, 6.0% initial ash) were chosen for use in this study. These coals are among a group of Ohio coals currently being evaluated for their physical beneficiation potential at Ohio University. Upon receipt from the Penn State Coal Sample Bank, the coals were carefully stored under nitrogen, were wet ground and vacuum dried. In performing the capillary rise experiments, the dried samples were put into glass tubes (120mm long x 10mm ID) with fritted glass bottoms, to form packed beds. A standard tapping procedure was adopted to insure that the packing, and hence the porosity, did not vary too much from one bed to the another. It was found that after 500 taps, dealt out in sets of 50 interspersed with the addition of more coal to the tube, the variation in the final height of sample in the column did not change more than 2mm (1.7% of total bed height). The tubes were weighed before and after the filling and the weight of sample per unit volume of the tube was computed. The sides of the tubes were marked with graduations, and the tubes placed vertically so that the bottom of the tube was just in contact with the liquid in a beaker. If the liquid were to wet the solid, it would rise up the tube at a rate dictated by Equation 4. This rise could clearly be observed. At the conclusion of the experiment, the tube was weighed once again and the weight of the liquid drawn up per unit volume of the tube, and the porosity were evaluated. It was found that for all the tests, the porosity fell within the range 0.5 ± 0.02.

The change in height of the liquid in the column was recorded as a function of time and an h^2 versus t graph plotted. A good straight line fit was observed in every case, and the reproducibility was very good (Figure 2). The D values were calculated using the slopes obtained from experiments performed with and without an external applied pressure. These values are depicted in Table 2. Also shown are the particle volume mean diameters which were measured using a Horiba CAPA 300 centrifugal particle size analyzer (the assumed particle density was 1.35 g/ml). Both sets of particle size readings show the same trend with the "capillary" readings being, on the average, 28% greater than the centrifugal sizing readings. The $\cos\theta$ and θ values for the three coals with Varsol and pentane are also computed, using the calculated D values. Young's equation (Equation 5) was applied to the data and the product, $\delta_{lv}\cos\theta$ calculated.

$$\delta_{sv} - \delta_{sl} = \delta_{lv}\cos\theta \qquad 5)$$

The term $\delta_{lv}\cos\theta$ represents the difference between the coal-air interfacial energy and the coal-oil interfacial energy, that is, the decrease in free energy that occurs when the coal is wetted by the oil. Calculated values for these three terms can be found in Table 3.

The three coals, PSOC 276, PSOC 305, and PSOC 751 have been subjected to oil agglomeration testing using No.2 fuel oil, Varsol, and pentane as the agglomerating oils. The results of several oil agglomeration tests are given in Table 4. A comparison of Tables 3 and 4 illustrate that the coal/oil combinations which yield the best ash reductions are also the combinations having the larger surface free energy decreases. Therefore, the wettability results do provide some indication of the oil agglomeration performance that may be expected for a given coal/oil combination.

TABLE 2

Particle Diameters.

Coal	Mean particle diameters, microns	
	From Capillary Calc.	From CAPA 300
PSOC 276	11.3	8.4
PSOC 305	11.9	9.5
PSOC 751	10.1	8.1
Standard Dev.	0.8	0.8

TABLE 3

Contact Angle Results.

Coal	No. 2 Fuel Oil			Varsol			Pentane		
	θ	$\cos\theta$	$\sigma_{lv}\cos\theta$	θ	$\cos\theta$	$\sigma_{lv}\cos\theta$	θ	$\cos\theta$	$\sigma_{lv}\cos\theta$
PSOC 276	74.6	0.26	7.3	83.3	0.12	3.3	83.7	0.11	2.0
PSOC 305	83.7	0.11	3.1	87.2	0.05	1.4	89.3	0.04	0.7
PSOC 751	79.8	0.18	5.0	84.6	0.09	2.4	85.8	0.07	1.2

Free energies reported in units of dyne/cm.

TABLE 4

Results of Oil Agglomeration Testing.

Coal	Oil	Feed Ash, wt%	Product Ash, wt%	% Ash Reduction
PSOC 276	No. 2	15.5	9.0	41.9
PSOC 276	Varsol	13.7	7.7	43.8
PSOC 276	Pentane	13.6	7.2	47.1
PSOC 305	No. 2	22.7	12.4	45.4
PSOC 305	Varsol	22.4	17.2	23.2
PSOC 305	Pentane	22.7	17.1	24.7
PSOC 751	No. 2	6.1	3.6	41.0
PSOC 751	Varsol	5.7	3.5	38.6
PSOC 751	Pentane	5.7	4.4	22.8

CONCLUSIONS

A modified Washburn technique of contact angle measurement has been proposed that does not suffer from some of the inadequacies of the original technique. Using the modified method, the decrease in free energy associated with the replacement of a solid-air interface by a solid-liquid interface can be measured. Such measurements are useful in predicting the efficiencies that may be expected in the oil agglomeration process and possibly in other surface-based physical beneficiation processes. Additional processing information, such as degree of mineral matter liberation, is required in order to make quantitative predictions of beneficiation performance.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the State of Ohio for its financial support. The authors would also like to thank the Penn State Coal Sample Bank for supplying the coal samples used and Dr. W. Kneller of the University of Toledo for his help in obtaining the mercury porosimetry data.

REFERENCES

1. Bartell, F.E., and Merril, E.J., J. Phys. Chem., 36, 1178 (1932); Bartell, F.E., and Whitney, C.E., ibid., p. 3115.
2. Washburn, E.W., Phys. Rev., 17, 273 (1921).
3. Heertjes, P.H., and Kossen, N.W.F., Powder Technology, 2, 33 (1967).
4. Neumann, A.W., and Good, R.J., in Surface and Colloid Science, Vol. 11, Good, R.J., and Stromberg, R.R., eds., Plenum, NY (1979).
5. Hiemenz, P.C., Principles of Colloid and Surface Chemistry, 2nd ed., Marcel Dekker, NY (1986).
6. Bird, R.B., Stewart, W.E., and Lightfoot, E.N., Transport Phenomena, John Wiley, NY (1960).
7. McCabe, W.L., and Smith, J.C., Unit Operations of Chemical Engineering, 3rd ed., McGraw-Hill, NY (1976).
8. Perry, R.H., and Chilton, C.H., eds., Chemical Engineers' Handbook, 5th ed., McGraw-Hill, NY (1973).

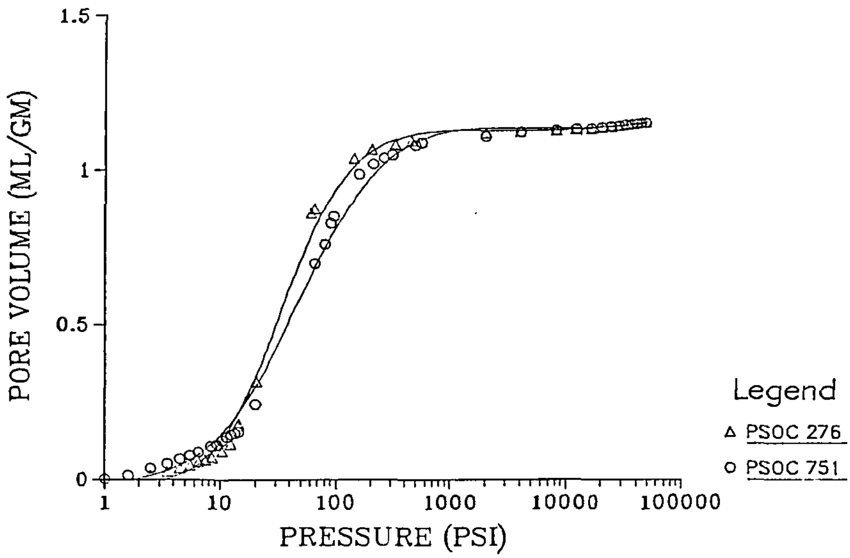

Figure 1. Mercury intrusion data for two Ohio coals.

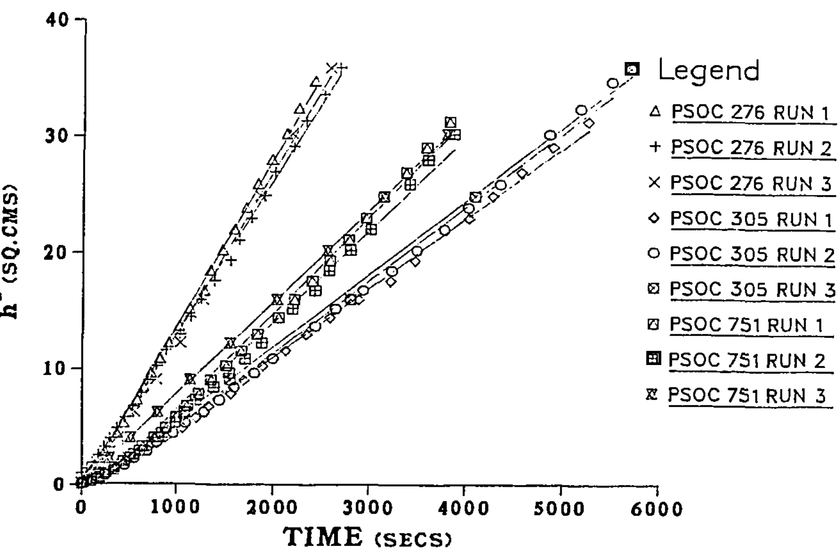

Figure 2. Capillary rise data for the intake of No. 2 Fuel oil by three Ohio coals. Three runs for each coal.